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A DENSITY FUCTIONAL THEORY (DFT) STUDY OF THE PROPOSED INSENSITIVE HIGH ENERGY DENSITY MATERIAL (IHEDM) 2-(NITROAMINOMETHYLENE)-4,5-DINITROCYCLOPENTA-3,5-DI-NITROAMINE (NDDN)

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14. ABSTRACT

A theoretical analysis of the proposed insensitive high energy density material (IHEDM) 2-(nitroaminomethylene)-4,5-dinitrocyclopenta-3,5-diene-1,3-di-nitroamine (NDDN) is reported. A Density Functional Theory (DFT) study was performed in order to determine the optimized structure and stability, as well as thermochemical aspects of NDDN. All calculations were performed using the Gaussian03 software with the Gaussview graphical user interface. Normal modes of vibration and heat of detonation of the proposed insensitive energetic material are calculated; the oxygen balance and energy density of the proposed IHEDM are also determined. Calculations were also performed on FOX-7; 2,4-dinitroimidazole (2,4-DNI); RDX, 2-methyl-4,5-dinitro-1,2,3-triazole-2-oxide (MDNTO); and HIVIX to enable comparison of the chosen explosive performance parameters to NDDN.

15. SUBJECT TERMS

2-(nitroaminomethylene)-4,5-dinitrocyclopenta-3,5-diene-1 ,3-di-nitroamine (NDDN); 2,4-dinitroimidazole (2,4-DNI); 1,1 -diamino-2,2-dinitroethene (DADNE, i.e., FOX-7); RDX; HMX; MDNTO (2-methyl-4,5-dinitro-1,2,3-triazole-2-oxide); Density Functional Theory (DFT); B3LYP; Vibrational modes; Heat of detonation; Oxygen balance (OB); energy density (molecular); Composite volumetric-energy density (CVED).

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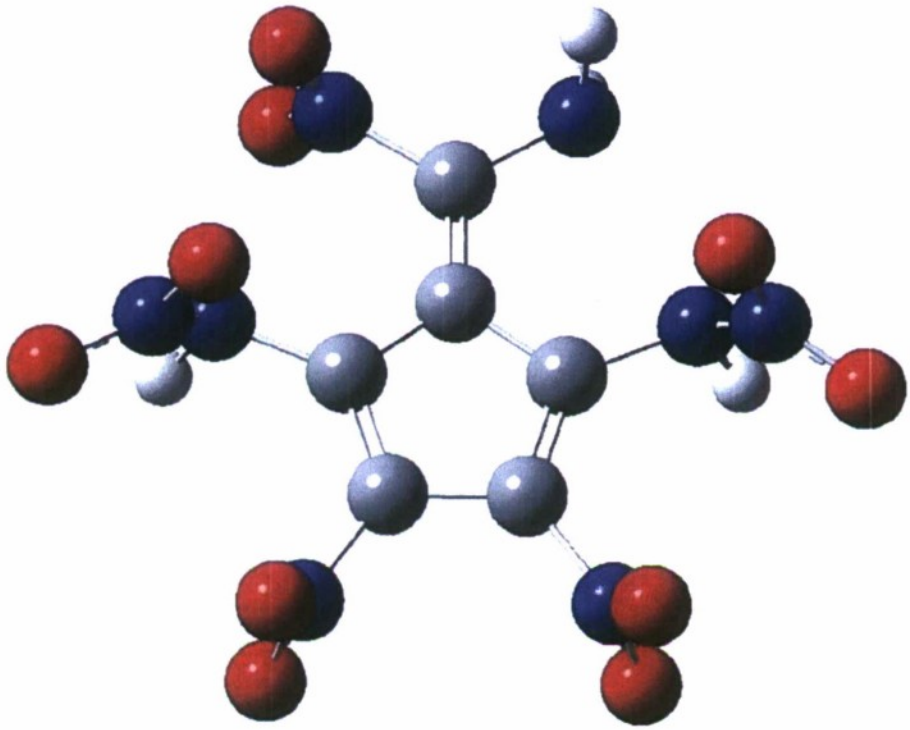
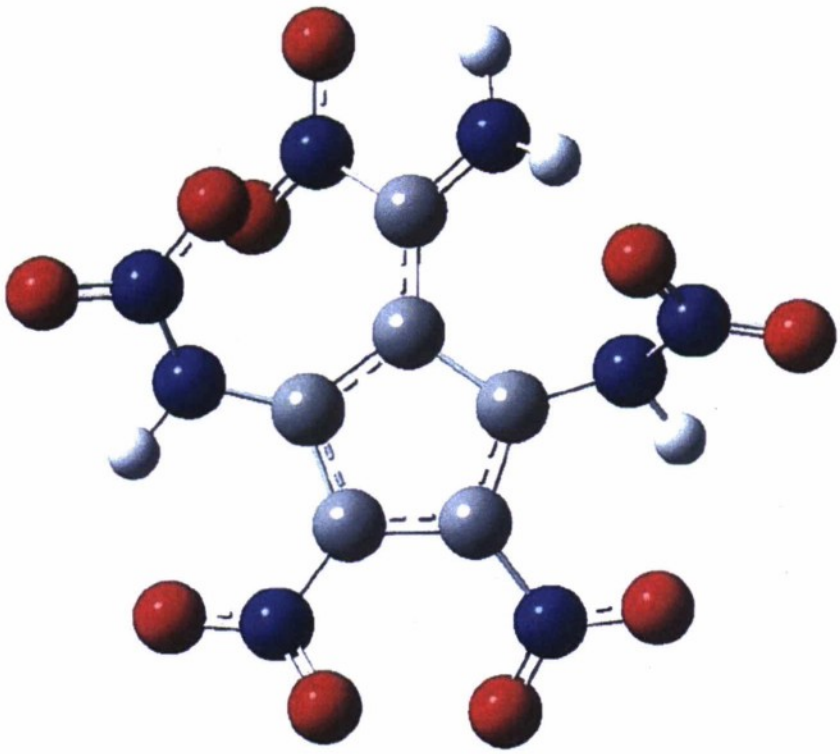
SUMMARY

The stability and thermochemistry of a proposed insensitive high energy density material (IHEDM) -- 2-(nitroaminomethylene)-4,5-dinitrocyclopenta-3,5-diene-1,3-di-nitroamine (NDDN) -- is assessed using the Density Functional Theory (DFT) as implemented in Gaussian03. The optimized structure of the proposed energetic, NDDN, is illustrated in fig. 1a and b. The DFT results demonstrate that NDDN is indeed stable on the molecular potential energy surface with energy density and heat of detonation characteristics superior to FOX-7, RDX, and HMX. In particular, NDDN possesses a molecular energy density 47% greater than 2,4-dinitroimidazole (2,4-DNI) and 19% greater than RDX, and a heat of detonation 38% greater than HMX. Gas-phase thermochemistry results and volumetric energy density calculations indicate that this molecule is superior overall to HMX; FOX-7; RDX; 2-methyl-4,5-dinitro-1,2,3-triazole-2-oxide (MDNTO); and 2,4-DNI and may also possess significant potential for applications where explosive or propellant properties may be pursued and tuned in a single molecular configuration.



Top view of initial (unoptimized) NDDN structure

Figure 1
NDDN



Top view of NDDN B3LYP/6-31g(d)-optimized structure

Figure 1
(continued)

INTRODUCTION

In organic chemistry, the structures of some rings of atoms are unexpectedly stable. Aromaticity is a chemical property in which a conjugated ring of unsaturated bonds, lone pairs, or empty orbitals exhibit stabilization stronger than would be expected by the stabilization of conjugation alone. It can also be considered a manifestation of cyclic delocalization and of resonance. Moreover, the presence of hydrogen bonding in molecules also signals greater stability than what would be expected. These characteristics ultimately equate to a general trend toward decreased impact and friction sensitivity when present in energetic materials.

The NDDN is expected to possess equivalent insensitivities due to availability of inter- and intra-molecular hydrogen bonds and electron delocalization with enhanced volumetric power characteristics due to the additional molar volume of decomposition products.

METHODS, ASSUMPTIONS, AND PROCEDURES

Computational details: DFT was applied in this study as implemented in Gaussian03. For the Kohn-Sham Hamiltonian, a generalized gradient approximation is included in Becke's exchange correlation functional B3LYP. This three-parameter hybrid functional was paired with a valence double-zeta polarized basis set; i.e., 6-31g(d). This pairing represents a reasonable level of theory and basis set complexity that duplicates gas-phase heats of formation and heats of reaction for CNOH-containing molecules with good to excellent accuracy and precision.

For calculation of the oxygen balance (OB), the following approach was used: for an explosive that contains some or all of the following atoms: aluminum, boron, carbon, calcium, chlorine, fluorine, hydrogen, potassium, nitrogen, sodium, and oxygen (with the formula Al_{al}, B_b, C_c, Ca_{ca}, Cl_{cl}, F_f, H_h, K_k, Na_{na}, O_o), the oxygen balance (OB%) will be

$$-\frac{32\{0.75al + 0.75b + 1c + 0.5ca - 0.25cl - 0.25f + 0.25h + 0.25k + 0n + 0.2na - 0.5o\}}{explosive\ molecular\ weight}\ x\ 100$$

where the indices - al, b, c, ca, cl, f, h, k, n, na, and o - denote the number of atoms of each element in a mole of the explosive composition. The contribution of nitrogen to the oxygen balance is zero, since it does not bind to the other elements.

The heats of reaction (i.e., detonation - ΔH°_{det}) for the respective molecules were determined as ΔH°_f (products) - ΔH°_f (reactants) using the thermochemical output from the Gaussian DFT calculations.

The molecular energy density values were calculated from the heats of reaction results and the molecular masses: Energy Density (KJ/gram) (KJ/mole) (moles/gram).

The explosion of one mole of NDDN produces 12-molar volumes, as can be seen from the stochiometrically balanced equation shown in the next section. These molar volumes at 0°C and atmospheric pressure form an actual volume of (12 moles)(22.4 L/mole) = 268.8 L. Using Charles' law, this volume can be calculated for other temperatures; for example, at 15°C (288.15K), $V_{15^\circ C}$ (22.4 L/mole)(288.15/273.15) = 23.64 L/mole. Therefore, at 15°C, the volume of gas produced by the explosive decomposition of one mole of NDDN is: $V_{15^\circ C}$ = (23.64 L/mole)(12 moles) = 283.7 L. As a measure of performance, the composite volumetric energy density (CVED, KJ-L/gram) = (Energy Density)(Volume of gas produced) was introduced. The CVED results are tabulated in table 2.

RESULTS AND DISCUSSION

The results of the normal mode analysis (fig. 2) for the proposed IHEDM structure yielded no imaginary frequencies for the 3N–6 vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of the NDDN molecule corresponds to at least a local minimum on the potential energy surface. Figure 2 also includes the specific infrared and Raman frequencies for future reference should the synthesis and characterization of NDDN be pursued.

In order to estimate the amount of energy available for release upon detonation, we need to apply the Kistiakowsky-Wilson rules, which state that (for an explosive with an oxygen balance (OB) not below -40%):

1. Carbon atoms are converted to CO
2. Any remaining oxygen is used to convert hydrogen atoms to H_2O
3. Any oxygen remaining after no. 2 is satisfied is used to convert CO to CO_2
4. All nitrogen atoms are converted to N_2

	1	2	3
	A	A	A
Frequencies --	40.2205	54.2274	60.2603
Red. masses --	12.8220	14.1654	14.4687
Frc consts --	0.0122	0.0245	0.0310
IR Inten --	0.2696	1.6384	0.1518
Raman Activ --	0.6378	1.1703	0.2310
Depolar (P) --	0.5935	0.3743	0.7486
Depolar (U) --	0.7449	0.5447	0.8562

	4	5	6
	A	A	A
Frequencies --	65.2403	71.2528	82.1161
Red. masses --	14.1189	11.7193	12.8501
Frc consts --	0.0354	0.0351	0.0511
IR Inten --	2.3919	0.7992	0.9186
Raman Activ --	3.3768	2.2212	2.4510
Depolar (P) --	0.4950	0.7165	0.6096
Depolar (U) --	0.6622	0.8348	0.7575

	7	8	9
	A	A	A
Frequencies --	90.8724	97.1502	118.9919
Red. masses --	15.0690	11.6543	11.3921
Frc consts --	0.0733	0.0648	0.0950
IR Inten --	1.4242	4.8060	2.1615
Raman Activ --	0.8561	5.4797	4.1864
Depolar (P) --	0.5411	0.7299	0.7455
Depolar (U) --	0.7022	0.8439	0.8542

	10	11	12
	A	A	A
Frequencies --	131.0205	142.5644	160.6964
Red. masses --	14.1147	9.6736	12.8031
Frc consts --	0.1428	0.1158	0.1948
IR Inten --	0.3329	1.7404	7.6538
Raman Activ --	0.8354	2.7622	0.5448
Depolar (P) --	0.7003	0.4433	0.7407
Depolar (U) --	0.8238	0.6143	0.8510

	13	14	15
	A	A	A
Frequencies --	182.9776	199.6519	211.0903
Red. masses --	13.6384	12.7726	14.7533
Frc consts --	0.2690	0.3000	0.3873
IR Inten --	2.3255	2.6161	3.4315
Raman Activ --	3.5403	2.6871	0.5418
Depolar (P) --	0.4196	0.6444	0.4903
Depolar (U) --	0.5912	0.7838	0.6580

	16	17	18
	A	A	A
Frequencies --	238.1001	261.2198	288.3314
Red. masses --	12.8716	7.6521	7.6825
Frc consts --	0.4299	0.3076	0.3763
IR Inten --	0.8424	7.3995	3.2340
Raman Activ --	6.8912	1.9555	2.9928
Depolar (P) --	0.1694	0.4080	0.2967
Depolar (U) --	0.2897	0.5796	0.4576

Figure 2
Vibrational frequencies (normal modes) of NDDN

	19	20	21
	A	A	A
Frequencies --	327.4994	333.1447	358.6960
Red. masses --	8.5377	11.5637	13.1316
Frc consts --	0.5395	0.7562	0.9955
IR Inten --	8.9168	1.9057	3.6936
Raman Activ --	1.6950	8.8357	1.8826
Depolar (P) --	0.7295	0.2276	0.7341
Depolar (U) --	0.8436	0.3709	0.8467

	22	23	24
	A	A	A
Frequencies --	367.3987	384.6006	406.0825
Red. masses --	10.9440	13.0952	7.4153
Frc consts --	0.8704	1.1413	0.7205
IR Inten --	2.8630	0.5872	0.6964
Raman Activ --	8.2802	1.8960	2.1150
Depolar (P) --	0.6060	0.4633	0.3724
Depolar (U) --	0.7546	0.6333	0.5427

	25	26	27
	A	A	A
Frequencies --	431.4174	456.6865	482.0004
Red. masses --	5.0364	10.7273	7.7415
Frc consts --	0.5523	1.3182	1.0597
IR Inten --	10.9569	0.6149	24.5997
Raman Activ --	3.1202	0.3971	1.7344
Depolar (P) --	0.7467	0.3796	0.7071
Depolar (U) --	0.8550	0.5503	0.8284

	28	29	30
	A	A	A
Frequencies --	562.0950	588.1004	606.8025
Red. masses --	10.3783	9.3183	3.6183
Frc consts --	1.9320	1.8989	0.7850
IR Inten --	5.8570	9.1201	9.9479
Raman Activ --	2.7047	2.6404	5.2422
Depolar (P) --	0.6981	0.5289	0.2634
Depolar (U) --	0.8222	0.6918	0.4170

	31	32	33
	A	A	A
Frequencies --	634.8467	649.8708	662.7837
Red. masses --	4.4393	2.2021	2.6360
Frc consts --	1.0541	0.5479	0.6822
IR Inten --	11.9570	91.1772	29.3569
Raman Activ --	4.9116	3.6268	4.6528
Depolar (P) --	0.7335	0.7327	0.4704
Depolar (U) --	0.8463	0.8457	0.6399

Figure 2
(continued)

	34	35	36
	A	A	A
Frequencies --	685.6373	702.5895	708.1724
Red. masses --	2.5096	6.0411	5.2843
Frc consts --	0.6951	1.7570	1.5614
IR Inten --	65.3439	9.4549	5.4385
Raman Activ --	1.1579	8.7904	3.8376
Depolar (P) --	0.6684	0.3625	0.1666
Depolar (U) --	0.8013	0.5321	0.2856

	37	38	39
	A	A	A
Frequencies --	731.2313	750.4892	757.7291
Red. masses --	2.9369	11.8731	7.8649
Frc consts --	0.9252	3.9401	2.6605
IR Inten --	37.5275	26.4467	9.2818
Raman Activ --	6.9169	0.4674	6.2790
Depolar (P) --	0.6545	0.7493	0.3033
Depolar (U) --	0.7912	0.8567	0.4654

	40	41	42
	A	A	A
Frequencies --	767.4133	773.4091	787.1838
Red. masses --	9.0291	11.7888	5.0229
Frc consts --	3.1329	4.1547	1.8338
IR Inten --	25.8503	8.2245	25.7864
Raman Activ --	13.5921	5.8327	9.6523
Depolar (P) --	0.6634	0.5018	0.2249
Depolar (U) --	0.7976	0.6683	0.3672

	43	44	45
	A	A	A
Frequencies --	804.7028	815.4206	846.6464
Red. masses --	8.1800	4.4824	2.6922
Frc consts --	3.1209	1.7560	1.1370
IR Inten --	3.4175	27.7492	67.7602
Raman Activ --	1.7660	30.4917	16.8194
Depolar (P) --	0.6322	0.1226	0.2728
Depolar (U) --	0.7746	0.2184	0.4287

	46	47	48
	A	A	A
Frequencies --	852.6867	861.4947	878.4279
Red. masses --	3.2893	2.1627	8.9400
Frc consts --	1.4091	0.9457	4.0644
IR Inten --	64.3149	68.2299	125.6700
Raman Activ --	5.9736	10.9597	4.1633
Depolar (P) --	0.1297	0.0845	0.6617
Depolar (U) --	0.2296	0.1559	0.7964

Figure 2
(continued)

	49	50	51
	A	A	A
Frequencies --	931.7512	1015.7531	1026.4674
Red. masses --	5.5198	3.5300	6.5576
Frc consts --	2.8234	2.1459	4.0708
IR Inten --	74.1715	99.3594	17.7599
Raman Activ --	18.1742	17.2519	26.9856
Depolar (P) --	0.1022	0.7275	0.3333
Depolar (U) --	0.1854	0.8423	0.5000

	52	53	54
	A	A	A
Frequencies --	1044.7612	1131.1733	1209.1205
Red. masses --	4.9420	6.2876	2.5590
Frc consts --	3.1782	4.7401	2.2043
IR Inten --	67.0061	0.5181	41.2695
Raman Activ --	18.1619	12.9082	16.8231
Depolar (P) --	0.1566	0.5318	0.3204
Depolar (U) --	0.2708	0.6943	0.4853

	55	56	57
	A	A	A
Frequencies --	1277.9646	1327.6400	1347.0805
Red. masses --	5.4339	11.5920	5.3559
Frc consts --	5.2288	12.0384	5.7263
IR Inten --	116.8081	457.7979	391.4172
Raman Activ --	59.8540	50.9228	167.6448
Depolar (P) --	0.6111	0.7499	0.1787
Depolar (U) --	0.7586	0.8571	0.3033

	58	59	60
	A	A	A
Frequencies --	1357.1637	1358.3239	1381.4572
Red. masses --	6.4026	5.2155	13.2288
Frc consts --	6.9482	5.6696	14.8746
IR Inten --	174.1773	253.4733	161.1706
Raman Activ --	256.1593	40.2693	144.8214
Depolar (P) --	0.2153	0.6082	0.1679
Depolar (U) --	0.3544	0.7564	0.2875

	61	62	63
	A	A	A
Frequencies --	1389.4797	1419.3324	1444.1232
Red. masses --	4.0400	9.8149	3.9775
Frc consts --	4.5955	11.6494	4.8873
IR Inten --	112.8569	90.3230	82.1438
Raman Activ --	58.7947	180.2683	16.0241
Depolar (P) --	0.6246	0.7064	0.5152
Depolar (U) --	0.7690	0.8279	0.6800

Figure 2
(continued)

	64	65	66
	A	A	A
Frequencies --	1467.5196	1498.0370	1557.2969
Red. masses --	2.3115	4.2112	2.9464
Frc consts --	2.9330	5.5680	4.2101
IR Inten --	78.4187	136.6105	164.4437
Raman Activ --	38.8669	153.4496	275.2326
Depolar (P) --	0.2708	0.7335	0.1939
Depolar (U) --	0.4262	0.8463	0.3248

	67	68	69
	A	A	A
Frequencies --	1567.6053	1578.9661	1614.6612
Red. masses --	5.3999	1.9092	11.7016
Frc consts --	7.8182	2.8044	17.9746
IR Inten --	62.6082	224.1857	298.5174
Raman Activ --	35.2618	128.7755	9.8069
Depolar (P) --	0.1963	0.1474	0.7423
Depolar (U) --	0.3282	0.2570	0.8521

	70	71	72
	A	A	A
Frequencies --	1638.4991	1687.6696	1695.6635
Red. masses --	11.7173	11.7671	6.2164
Frc consts --	18.5341	19.7467	10.5310
IR Inten --	119.9400	457.6405	370.8460
Raman Activ --	28.1588	4.0576	1.0291
Depolar (P) --	0.2861	0.7377	0.7127
Depolar (U) --	0.4449	0.8490	0.8323

	73	74	75
	A	A	A
Frequencies --	1721.1699	1733.2044	3337.7233
Red. masses --	4.6617	3.7255	1.0643
Frc consts --	8.1366	6.5938	6.9861
IR Inten --	211.2769	331.6401	369.2905
Raman Activ --	2.1084	1.5244	105.9806
Depolar (P) --	0.7467	0.7498	0.3356
Depolar (U) --	0.8550	0.8570	0.5026

	76	77	78
	A	A	A
Frequencies --	3441.0439	3456.7584	3576.9536
Red. masses --	1.0749	1.0795	1.0902
Frc consts --	7.4990	7.6002	8.2183
IR Inten --	97.8640	134.8380	292.8028
Raman Activ --	55.6355	75.7838	88.8508
Depolar (P) --	0.1247	0.1134	0.3367
Depolar (U) --	0.2217	0.2037	0.5038

Figure 2
(continued)

Applying these rules to NDDN, FOX-7, RDX, and HMX, the following ratios of detonation products are predicted:

NDDN:	$C_6N_8O_{10}H_4$	$4CO + 2H_2O + 2CO_2 + 4N_2$
FOX-7:	$C_2N_4O_4H_4$	$2CO + 2H_2O + 2N_2$
2,4-DNI:	$C_3N_4O_4H_2$	$3CO + 1H_2O + 2N_2$
RDX:	$C_3N_6O_6H_6$	$3CO + 3H_2O + 3N_2$
HMX:	$C_4O_5N_5H_3$	$4CO + 4H_2O + 4N_2$
MDNTO:	$C_3O_5N_5H_3$	$2CO + 3/2(H_2O) + 5/2(N_2) + ¾(CO_2) + ¼(C)$

From this information and the DFT calculated heats of formation of the reactants and products, the heat of reaction (i.e., detonation) can be determined as follows:

$\Delta H^\circ_{det}(NDDN) = [4\Delta H^\circ_f(CO) + 2\Delta H^\circ_f(H_2O) + 2\Delta H^\circ_f(CO_2) + 4\Delta H^\circ_f(N_2)] - [-\Delta H^\circ_f(NDDN)]$

$\Delta H^\circ_{det}(FOX\text{-}7) = 2\Delta H^\circ_f(CO) + 2\Delta H^\circ_f(H_2O) + 2\Delta H^\circ_f(N_2) - [-\Delta H^\circ_f(FOX\text{-}7)]$

$\Delta H^\circ_{det}(2,4\text{-}DNI) = 3\Delta H^\circ_f(CO) + 1\Delta H^\circ_f(H_2O) + 2\Delta H^\circ_f(N_2) - [-\Delta H^\circ_f(2,4\text{-}DNI)]$

$\Delta H^\circ_{det}(RDX) = 3\Delta H^\circ_f(CO) + 3\Delta H^\circ_f(H_2O) + 3\Delta H^\circ_f(N_2) - [-\Delta H^\circ_f(RDX)]$

$\Delta H^\circ_{det}(HMX) = 4\Delta H^\circ_f(CO) + 4\Delta H^\circ_f(H_2O) + 4\Delta H^\circ_f(N_2) - [-\Delta H^\circ_f(HMX)]$

$\Delta H^\circ_{det}(MDNTO) = 2\Delta H^\circ_f(CO) + 3/2\Delta H^\circ_f(H_2O) + 5/2\Delta H^\circ_f(N_2) + 3/4\Delta H^\circ_f(CO_2) + ¼(C) - [-\Delta H^\circ_f(MDNTO)]$

The heats of detonation for these molecules, as well as their products, are reported as the "sum of electronic and thermal energies" in atomic units (i.e., Hartrees) via the thermochemistry output calculated at the B3LYP/6-31g(d) level of theory (tables 1 and 2).

Table 1
Thermochemistry output for detonation products

	MW	ΔH°_f(au)*
CO_2	44	-188.567
CO	28	-113.302
H_2O	18	-76.385
N_2	28	-109.516
C	12	-37.844

*Sum of electronic and thermal energies as reported from the Gaussian03 DFT thermochemistry results.

Table 2
ADAND, FOX-7, RDX, HMX, MDNTO, and 2,4-DNI thermochemistry output and theoretical performance parameters

	ΔH°_{f} (au)*	MW	OB (%)	ΔH°_{det} (au/KJ/mole)	Energy density (KJ/g)	Volume (L)	CVED (KJ-L/g)
ADAND	-1420.518	348	-27.6	-0.658/-1728	5.0	283.68	1418
FOX-7	-598.208	148	-21.6	-0.198/-519	3.5	141.84	496
2,4-DNI	-635.118	158	-30.4	-0.205/-538	3.4	141.84	482
RDX	-897.253	222	-21.6	-0.356/-935	4.2	212.76	894
HMX	-1196.336	296	-21.6	-0.476/-1250	4.2	283.68	1191
MDNTO	-765.549	189	-1.3	-0.310/-814	4.3	159.57	686

*Sum of electronic and thermal energies as reported from the Gaussian03 DFT thermochemistry results.

Note: Volume of gases calculated at 15°C.

Note that these calculations are based on rather idealized gas-phase enthalpies, and in reality, other factors such as phase transition from solid state to gaseous state, crystal and crystal packing density will be important. The point is that the ΔH°_{det} calculations are not necessarily to be taken in the absolute sense, but considered as a relative trend. In this way, more meaningful conclusions can be extracted from the data.

CONCLUSIONS

The Density Functional Theory results of this study indicate that the newly proposed high energy density material, 2-(nitroaminomethylene)-4,5-dinitrocyclopenta-3,5-diene-1,3-di-nitroamine (NDDN), has a molecular energy density nearly 43% greater than FOX-7 and 19% greater than either RDX or HMX. Further, the composite volumetric energy density of NDDN is approximately 194% greater than 2,4-dinitroimidazole, 186% greater than FOX-7, and 19% greater than HMX. The optimized structure is stable on the molecular potential energy surface, as evidenced by the absence of any imaginary frequencies.

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